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(54) DIAPHRAGM FOR SOLID HIGH MOLECULAR ELECTROLYTE FUEL CELL

(57)Abstract:

PROBLEM TO BE SOLVED: To develop a diaphragm for a solid high molecular fuel cell, wherein the diaphragm has sufficient physical strength, small electric resistance, and low gas permeability.

SOLUTION: A polyolefin based porous film, preferably a polyolefin based porous film having average molecular weight of 100,000 to 450,000 is used for a base material of a diaphragm for a solid high molecular electrolyte fuel cell. The diaphragm is formed of an anode ion exchange film wherein anode ion exchange resin is stuffed in porous areas thereof and its electric resistance in 1 mol/L of sulfuric acid aqueous solution is not more than 0.20 Ω.cm², and permeation coefficient of hydrogen gas at 50 degrees centigrade is not more than 3.0×10^{-8} cm³(STP).cm.cm⁻².s⁻¹.cmHg⁻¹.

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CLAIMS

[Claim(s)]

[Claim 1] The diaphragm for solid-state polyelectrolyte mold fuel cells which uses polyolefine system porous membrane as a base material, and it comes to fill up the hole section cation exchange resin, and the electric resistance in a 1 mol/L-sulfuric-acid water solution is two or less 0.20ohm and cm, and is characterized by the transmission coefficient of the hydrogen gas in 50 degrees C consisting of cation exchange membrane which is $3.0 \times 10^{-8} \text{cm}^3$ (STP), $\text{cm} \cdot \text{cm}^{-2}$, s^{-1} , and less than [cmHg $^{-1}$].

[Claim 2] The diaphragm for solid-state polyelectrolyte mold fuel cells according to claim 1 whose weight average molecular weight of polyolefine system porous membrane is 100,000-450,000.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the diaphragm for solid-state polyelectrolyte mold fuel cells which consists of a diaphragm for polymer electrolyte fuel cells, and cation exchange membrane which uses polyolefine system porous membrane as a base material in detail.

[0002]

[Description of the Prior Art] A fuel cell is a generation-of-electrical-energy system which takes out chemical energy when a fuel and an oxidizer are supplied continuously and these react as power. A fuel cell is divided roughly by the class of electrolyte used for this with a phosphoric-acid mold with a comparatively low operating temperature, a solid-state macromolecule mold, the melting carbonate mold that operates at an elevated temperature, and a solid oxide type.

[0003] it be make to act as a fuel cell by join the gas diffusion electrode with which the catalyst be **** (ed) by both sides of the diaphragm of the solid-state macromolecule on which a polymer electrolyte fuel cell act as an electrolyte in these , supply the oxygen content gas which be oxidizers , such as oxygen and air , respectively to ** of the side to which the gas diffusion electrode of another side exist the hydrogen which be a fuel in ** (combustion chamber) of the side in which one gas diffusion electrode exist , and connect an external load circuit between ring main diffusion electrodes .

[0004] The basic structure of such a polymer electrolyte fuel cell is shown in drawing 1 . the inside of drawing, and (1) -- in a cell septum and (2), a combustion chamber side gas diffusion electrode and (5) show an oxidizer room side gas diffusion electrode, and, as for a fuel gas circulation hole and (3), (6) shows the solid-state polyelectrolyte film, as for an oxidizer gas circulation hole and (4). In this polymer electrolyte fuel cell, by the combustion chamber (7), a proton (hydrogen ion) and an electron generate from the supplied hydrogen gas, and this proton conducts the inside of a solid-state polyelectrolyte (6), moves to the oxidizer room (8) of another side, reacts with the oxygen in air or oxygen gas, and generates water. At this time, when the electron generated with the combustion chamber side gas diffusion electrode (4) moves to an oxidizer room side gas diffusion electrode (5) through an external load circuit, electrical energy is obtained.

[0005] In the polymer electrolyte fuel cell of such structure, cation exchange membrane is usually used for the above-mentioned diaphragm. And it is required for this cation exchange membrane small [electric resistance], high [water retention], that gas permeability is low, stable to long-term use, that physical reinforcement should be strong, etc.

[0006] Conventionally, the perfluorocarbon-sulfonic-acid film is mainly used as a cation exchange membrane used as a diaphragm for polymer electrolyte fuel cells. However, although this film was excellent in chemical stability, reduction of the electric resistance by thin-film-izing was [that desiccation of cation exchange membrane arises and the conductivity of a proton tends to fall] difficult for it, since still more nearly physical reinforcement was also inadequate, since water holding capacity was inadequate. Furthermore, the perfluorocarbon-sulfonic-acid film was expensive.

[0007]

[Problem(s) to be Solved by the Invention] On the other hand to JP,1-22932,A, as a diaphragm for polymer electrolyte fuel cells The cation exchange membrane with which weight average molecular weight comes to fill up cation exchange resin all over 500,000 or more holes of the polyolefine system porous membrane of the amount of macromolecules is indicated. As the manufacture approach Make a solvent dissolve cation exchange resin in the above-mentioned porous membrane, it is made to sink in, the approach of making a solvent removing, the monomer of cation exchange resin, etc. are infiltrated into the above-mentioned

porous membrane after that, the method of performing the polymerization of the above-mentioned raw material monomer etc. is indicated after that.

[0008] However, when this cation exchange membrane infiltrated into the above-mentioned porous membrane the solution which cation exchange resin dissolves, and its raw material monomer since a base material is the polyolefine of the amount of macromolecules although physical reinforcement was good, this porous membrane did not fully swell it, but it had the problem into which these do not fully enter to the details in a membranous hole. By the approach of infiltrating the solution of cation exchange membrane especially, since a solvent was removed after sinking in, the volume change of packing arose and the restoration nature to the hole section details of the above-mentioned porous membrane was falling further. Moreover, it was difficult to have made it fill up also with the approach of infiltrating a raw material monomer, densely to the hole section details, since these monomers are hyperviscosity in many cases.

[0009] Therefore, the cation exchange membrane obtained by the above-mentioned approach was that from which it does not fill up with cation exchange resin densely to the hole details of a base material, and the permeability of gas is large, therefore it cannot fully suppress that the hydrogen gas of a combustion chamber is spread in an oxidation room side when it is used as said diaphragm for fuel cells, and a big cell output is not obtained. Moreover, ion exchange capacity was low and the electric resistance of ion exchange capacity was also high.

[0010] As mentioned above, it was a big technical problem to have sufficient physical reinforcement and to develop a polymer electrolyte fuel cell diaphragm with low gas permeability small [electric resistance].

[0011]

[Means for Solving the Problem] this invention persons have continued research wholeheartedly in order to solve the above-mentioned technical problem. Consequently, polyolefine system porous membrane was used as the base material, and electric resistance is small, and it succeeds in gas permeability developing low cation exchange membrane, and came to complete this invention.

[0012] That is, this invention is a diaphragm for solid-state polyelectrolyte mold fuel cells which uses polyolefine system porous membrane as a base material, and it comes to fill up the hole section cation exchange resin, and the electric resistance in a 1 mol/L-sulfuric-acid water solution is two or less 0.20ohm and cm, and is characterized by the transmission coefficient of the hydrogen gas in 50 degrees C consisting of cation exchange membrane which is $3.0 \times 10^{-8} \text{cm}^3$ (STP), cm⁻², s⁻¹, and less than [cmHg⁻¹].

[0013]

[Embodiment of the Invention] As for the cation exchange membrane used in this invention, the free passage hole of polyolefine system porous membrane is filled up with cation exchange resin, and, as for usual, it fills up with the so-called ion exchange resin of a hydrocarbon system completely substantially. That is, the high hydrocarbon system ion exchange resin of the hydration force is the cation exchange membrane of the gestalt distributed to polyolefine system porous membrane, and since the restoration nature of ion exchange resin is high, this cation exchange membrane can be set as the range of a request of electric resistance and the transmission coefficient of hydrogen gas by adjusting ion exchange capacity and fixed ion concentration.

[0014] As polyolefine which is raw material resin of porous membrane, the homopolymer of the alpha olefin of carbon numbers 2-8, other alpha olefins, or a copolymer with other monomers which can be copolymerized is suitably mentioned for ethylene, a propylene, 1-butene, 1-pentene, 1-hexene, a 3-methyl-1-butene, 4-methyl-1-pentene, a 5-methyl-1-heptene, etc. 90% of the weight or more of a thing has the desirable content of the monomer based on an alpha olefin. In such polyolefines, polyethylene and polypropylene are desirable and especially polyethylene is desirable.

[0015] the weight average molecular weight of polyolefine -- 10,000-450,000 -- suitable -- 100,000-450,000 -- 150,000-400,000 are still more suitably desirable. By using the polyolefine of the above-mentioned weight average molecular weight, it becomes possible for porous membrane to become what has low bloating tendency, and for you to make it more densely filled up with this monomer constituent to the hole details in the manufacture approach of the cation exchange membrane mentioned later at the time of sinking [of the monomer constituent for manufacturing cation exchange resin] in.

[0016] In addition, backing according [such polyolefine system porous membrane] to blanket-like objects, such as a product made from polypropylene system fiber, further may be performed.

[0017] 0.1-5 micrometers, suitably, the average aperture of the hole of the above-mentioned polyolefine system porous membrane is 0.1-1 micrometer, and 40 - 90% of thing of voidage is more preferably desirable [an aperture] 30 to 95%. Since electric resistance increases when an average aperture is 0.1 micrometers or less, and a mechanical strength becomes low when an average aperture is 5 micrometers

or less, it is not desirable. Moreover, since electric resistance increases when voidage is 30% or less, and a mechanical strength becomes low when voidage is 95% or more, it is not desirable.

[0018] Furthermore, as for polyolefine system porous membrane, what usually has the thickness of 5-100 micrometers from a viewpoint which gives the viewpoint which suppresses electric resistance low, and a mechanical strength required as a supporting lamella is desirable, and what has 10-70 micrometers more preferably is desirable. That to which such polyolefine system porous membrane porosity-ized the polyolefine system film by the extending method etc. is used.

[0019] As for the diaphragm for solid-state polyelectrolyte mold fuel cells of this invention, the hole section of the above-mentioned polyolefine system porous membrane is filled up with cation exchange resin. Although it is not limited especially if it is the functional group which can serve as negative charge in the inside of a water solution as a cation-exchange radical of cation exchange resin, a sulfonic group, a carboxylic-acid radical, a phosphonic acid radical, etc. are mentioned, among these, specifically, especially a sulfonic group is desirable.

[0020] Since the thickness of said extent can use thin porous membrane as a base material in the cation exchange membrane used by this invention, the electric resistance in a 1 mol/L-sulfuric-acid water solution is the small value of 0.05-0.15ohm and cm² suitably two or less 0.20 ohm-cm, and it is advantageous as a diaphragm for cells.

[0021] And since the restoration nature of the cation exchange resin to the hole section of the porous membrane of a base material is high, the permeability of gas is very small [cation exchange membrane], while the cation exchange membrane used by this invention is film with electric resistance small like the above. namely, the transmission coefficient of the hydrogen gas in 50 degrees C -- 3.0x10⁻⁸cm³ (STP), cm^{-cm-2}, s⁻¹, and cmHg⁻¹ is 0.5-2.0x10⁻⁸cm³ (STP), cm^{-cm-2}, s⁻¹, and cmHg⁻¹ suitably one or less. Thus, since the transmission coefficient of hydrogen gas is small, that the supplied hydrogen gas penetrates a diaphragm and is spread in oxygen gas can prevent the diaphragm for solid-state polyelectrolyte mold fuel cells of this invention which consists of this cation exchange membrane good, and the cell of a high output is obtained.

[0022] In addition, generally the cation exchange membrane used by this invention which has the transmission coefficient of the above-mentioned hydrogen gas has the value of 2.0x10⁻⁸cm³ (STP), cm^{-cm-2}, s⁻¹ and less than [cmHg⁻¹], and also 0.3-1.5x10⁻⁸cm³ (STP), cm^{-cm-2}, s⁻¹ and cmHg⁻¹ as a transmission coefficient of the oxygen gas in 50 degrees C. Therefore, transparency of the diaphragm of oxygen gas can also prevent the polymer electrolyte fuel cell diaphragm of this invention good.

[0023] Furthermore, as for the cation exchange membrane used by this invention, it is desirable that the viewpoint which maintains electric resistance at the above-mentioned range to cation exchange capacity is 0.5 - 3.0 mmol/g suitably 0.2 to 5.0 mmol/g.

[0024] Moreover, as for water content, it is suitably desirable that it is 40% or more 30% or more so that it may be hard to produce the conductive fall of the proton by desiccation. Generally water content is held at about 30 - 90%. In order to obtain the water content of such range, it is controllable by the class, the cation exchange capacity, and the degree of cross linking of the cation exchange resin which exists in the hole section of porous membrane.

[0025] Although the cation exchange membrane which has such description may be manufactured by what kind of approach, generally it is manufactured by the following approaches. That is, after making it sink in, carrying out reduced pressure deaeration of the monomer constituent which consists of the monomer, cross-linking monomer, and polymerization initiator which have the functional group or cation-exchange radical which can introduce a cation-exchange radical at polyolefine system porous membrane, the polymerization of the monomer constituent is carried out and the approach of introducing a cation-exchange radical if needed is mentioned.

[0026] It is used in this manufacture approach, without limiting especially the hydrocarbon system monomer used in manufacture of conventionally well-known cation exchange resin as a monomer which has the monomer or cation-exchange radical which has the functional group which can introduce cation exchange membrane. Specifically as a monomer which has the functional group which can introduce a cation-exchange radical, styrene, vinyltoluene, a vinyl xylene, alpha methyl styrene, vinyl naphthalene, alpha-halogenation styrene, etc. are mentioned. Moreover, as a monomer which has a cation-exchange radical, phosphonic acid system monomers, such as carboxylic-acid system monomers, such as sulfonic-acid system monomers, such as a styrene sulfonic acid, a vinyl sulfonic acid, and alpha-halogenation vinyl sulfonic acid, a methacrylic acid, an acrylic acid, and a maleic anhydride, and a vinyl phosphoric acid, those salts, and ester are used.

[0027] Moreover, especially as a cross-linking monomer, although not restricted, divinyl compounds, such

as divinylbenzenes, a divinyl sulfone, a butadiene, a chloroprene, divinyl biphenyl, trivinylbenzene, divinyl naphthalene, a diaryl amine, and a divinyl pyridine, are used, for example.

[0028] In this invention, these monomers, other monomers which can be copolymerized, and plasticizers other than the monomer which has the monomer or cation-exchange radical which has the functional group which can introduce the above-mentioned cation-exchange radical, or a cross-linking monomer may be added if needed. As other monomers carried out like this, styrene, acrylonitrile, methyl styrene, an acrolein, a methyl vinyl ketone, a vinyl biphenyl, etc. are used, for example. Moreover, as plasticizers, dibutyl phthalate, dioctyl phthalate, dimethyl isophthalate, a dibutyl horse mackerel peat, triethyl SHITORETO, acetyl tributyl citrate, dibutyl sebacate, etc. are used.

[0029] Next, as a polymerization initiator in this invention, a well-known thing is conventionally used especially without a limit. As an example of such a polymerization initiator, organic peroxide, such as octanoyl peroxide, lauroyl peroxide, t-butylperoxy2-ethylhexanoate, benzoyl peroxide, t-butylperoxy isobutyrate, t-butyl peroxy laurate, t-hexyl peroxy benzoate, and G t-butyl peroxide, is used.

[0030] In this invention, the blending ratio of coal of each component which constitutes a monomer constituent in order to attain the purpose of this invention, generally As opposed to the monomer 100 weight section which has the monomer or cation-exchange radical which has the functional group which can introduce a cation-exchange radical It is suitable to carry out 0-50 weight section use of the cross-linking monomer to the above-mentioned monomer, when adding the 0 - 100 weight section and plasticizers for 1 - 40 weight section, and these monomers and other monomers which can be copolymerized suitably, 0.1 - 50 weight section and. Moreover, it is desirable 0.1 - 20 weight section and to carry out 0.5-10 weight section combination of the polymerization initiator suitably to the monomer 100 weight section which has the monomer or cation-exchange radical which has the functional group which can introduce a cation-exchange radical.

[0031] Especially the restoration approach of the above-mentioned monomer constituent to the polyolefine system porous membrane which is a base material is not limited. For example, what is necessary is just to make it sink in, carrying out reduced pressure deaeration of the monomer group living thing at polyolefine system porous membrane. If it deaerates and infiltrates filling up high density with the above-mentioned monomer constituent to the details of the hole section of polyolefine system porous membrane under reduced pressure in this way to being difficult, it will become possible to be filled up with a monomer constituent without a clearance to these hole section details, as described above. And the cation exchange membrane obtained by carrying out the polymerization of the monomer constituent turns into film with very low gas permeability which said invention in this application specifies after this sinking in.

[0032] Here, sinking-in processing while [above-mentioned] carrying out reduced pressure deaeration is contacted under the reduced pressure to polyolefine system porous membrane of a monomer constituent, and, specifically, is performed by returning a pressure to atmospheric pressure. For example, polyolefine system porous membrane is immersed in the monomer mixture which put the monomer constituent into the method of introducing into a container and infiltrating it until it returns to atmospheric pressure, or the container after putting polyolefine system porous membrane into the container and changing into a reduced pressure condition with a vacuum pump, and after carrying out reduced pressure deaeration of the gas in a hole with a vacuum pump, the approach of returning to atmospheric pressure is mentioned. Whenever [reduced pressure / when decompressing] has a desirable pressure until a monomer boils under 7kPa - working temperature, and it is desirable to choose from the range of 2kPa-0.1kPa especially. What is necessary is for the temperature at the time of sinking in to have common 20 degrees C or less, and just to usually choose sinking-in time amount suitably in the range for 5 - 60 minutes.

[0033] In order to postpolymerize, the approach of inserting into films, such as polyester, generally and carrying out a temperature up from ordinary temperature under pressurization which the above-mentioned polyolefine system porous membrane was made to fill up with a monomer constituent is desirable. What is necessary is for such polymerization conditions not to be influenced by the presentation of the class of polymerization initiator which involves, and a monomer constituent etc., not to limit them by the way, and just to choose them suitably.

[0034] The filmy material which a polymerization is carried out as mentioned above and obtained can introduce the cation-exchange radical of a request of this by processing of well-known sulfonation, the Krol sulfonation, phosphonium-izing, hydrolysis, etc. if needed, and can use it as cation exchange membrane.

[0035] this invention -- setting -- the above -- a well-known structure thing can apply the solid oxide fuel cell for which the cation exchange membrane of description is used as a diaphragm that there is no limit in any way. Usually, it is common to be applied to what has structure as shown in above mentioned drawing

1.

[0036]

[Effect of the Invention] Like the above explanation, the diaphragm for solid-state polyelectrolyte mold fuel cells of this invention has low electric resistance, and the cation exchange resin which constructed the bridge over the hole section of polyolefine system porous membrane consists of cation exchange membrane with which it filled up densely without a clearance to details. Therefore, the permeability of gas is very low. Moreover, since polyolefine system porous membrane is a base material, it excels also in dimensional stability or chemical resistance.

[0037] therefore, ** --- the crossover of a fuel and an oxidizing agent is controlled and, as for the fuel cell obtained using the diaphragm for solid-state polyelectrolyte mold fuel cells of this invention which has description [like], a high cell output is obtained. And increase of contact resistance with the electrode accompanying swelling contraction is suppressed, and heating sticking by pressure of the gas diffusion electrode can be carried out further there is no adhesive agent in this cation exchange membrane, and good again.

[0038]

[Example] Although an example and the example of a comparison are hereafter hung up and explained in order to explain this invention still more concretely, this invention is not limited to these examples.

[0039] In addition, the property of the cation exchange membrane shown in an example and the example of a comparison shows the value measured by the following approaches.

(1) Cation exchange capacity;

After being immersed in 1 mol/L-HCl for 10 hours or more and using cation exchange membrane as a hydrogen ion mold, the quantum of the hydrogen ion which was made to permute by the sodium ion mold and separated by 1 mol/L-NaCl was carried out with potentiometric titration equipment (COMTITE-900, Hiranuma Sangyo Co., Ltd. make) (Amol).

[0040] Next, reduced pressure drying of the same cation exchange membrane was carried out at 60 degrees C for 5 hours, and the weight was measured (Wg). Cation exchange capacity was calculated by the degree type.

Cation exchange capacity = Ax1000/W [the mmol/g-desiccation film]

(2) Cation exchange membrane was placed in the center of the two-room cel equipped with the electric resistance platinum electrode, and 25-degree C 3 mol/L sulfuric-acid water solution was filled in the cel. The Luggin capillary was prepared in the both sides of cation exchange membrane, and liquid junction was carried out to the reference electrode with the salt bridge. The potential (bV) when passing the current of 100 mA/cm², without inserting the potential (aV) and the film when passing the current of 100 mA/cm² on both sides of the film was measured. The electric resistance of cation exchange membrane was searched for from the degree type.

[0041]

Electric resistance = 1000x (a-b)/100 [omegacm²]

(3) After having been immersed in 1 mol/L-HCl for 4 hours or more, using water content cation exchange membrane as the hydrogen ion mold and fully rinsing it with ion exchange water, the film was taken out, surface moisture was wiped off by KIMUWAIPU etc., and the weight at the time of humidity (Wg) was measured. Next, reduced pressure drying of the film was carried out at 60 degrees C for 5 hours, and the weight at the time of desiccation (Dg) was measured. It asked for the water content of cation exchange membrane by the degree type.

[0042]

Water content = 1000x (W-D) / D [%]

(4) As a measuring method of a gas transmission coefficient gas transmission coefficient, the gas radiographic examination machine by the U-tube-construction mercury manometer (based on JIS Z 1707) was used. In 50 degrees C, the gas radiographic examination machine was equipped with the cation exchange membrane used for measurement by the moisture state. Moreover, the oxygen or hydrogen maintained at saturation temperature in 50 degrees C was used for the gas used for measurement. It asked for the gas transmission coefficient by the degree type.

[0043]

P=(p/t)x(1/A) x {1/(Pa-Pb)}

P: Gas transmission coefficient (cm³ (STP), cm-cm⁻², s⁻¹, and cmHg⁻¹)

p: The amount of gas transparency (cm³ (STP))

t: measuring time (s)

l: Cation-exchange-membrane thickness (cm)

A: Gas transparency area (cm²)

Pa: High-tension-side gas pressure (cmHg)

Pb: Low-tension side gas pressure (cmHg)

(5) On carbon paper of 80% of void contents which carried out water-repellent treatment by fuel cell output voltage polytetrafluoroethylene, what mixed 5% solution (the Du Pont make, trade name NAFION) of water with the carbon black of **** of 30 % of the weight of platinum and the alcohol of perfluorocarbon sulfonic acid was applied, reduced pressure drying was carried out at 80 degrees C for 4 hours, and it considered as the gas diffusion electrode.

[0044] Next, after setting the above-mentioned gas diffusion electrode to both sides of the cation exchange membrane to measure and carrying out a heat press for 100 seconds under 150 degrees C and pressurization with a pressure of 100kg/cm², it was left for 2 minutes at the room temperature. It included in the fuel cell cel which shows this to drawing 1, and the output voltage at the time of 200 mL/min and 400 mL/min was measured for oxygen with pressure 2 atmospheric pressure, a fuel cell cel temperature [of 50 degrees C], and a humidification temperature of 50 degrees C, and hydrogen, respectively.

(6) Thermal resistance (contraction)

After leaving the sample film for measurement which carried out predrying in the 50-degree C dryer for 1 hour in a 160-degree C dryer for 30 minutes, it took out from the dryer, the dimension was measured and contraction was searched for by the following formulas.

[0045] S=100x (La-Lb)/LaS: Contraction (%)

La: The die length of the film dried in the 50 degree C dryer (cm)

Lb: The die length of the film left in the 160 degree C dryer for 30 minutes (cm)

According to the presentation table having shown in one to example 6 table 1, various monomers etc. were mixed and the monomer constituent was obtained. 400g of obtained monomer constituents was put into the glassware of 500mL(s), and the polyolefine system porous membrane (A, B, C, every 20cmx 20cm) of weight average molecular weight 350,000 was immersed.

[0046] Next, glassware was made reduced pressure for 10 minutes to the pressure of 0.7kPa(s) with the vacuum pump, after carrying out reduced pressure deaeration, it returned to ordinary pressure and the hole of polyolefine system porous membrane was filled up with the monomer constituent. Then, polyolefine system porous membrane was taken out out of the monomer constituent, and after covering the both sides of polyolefine system porous membrane by making 100-micrometer polyester film into a remover, the heating polymerization was carried out under 3kg/cm² nitrogen pressurization for 80-degree-C 5 hours.

[0047] The obtained filmy material was immersed for 45 minutes at 40 degrees C into the 1:1 mixture of 98% concentrated sulfuric acid and the chlorosulfonic acid of 90% or more of purity, and sulfonic acid type cation exchange membrane was obtained.

[0048] The thickness of such sulfonic acid type cation exchange membrane, cation exchange capacity, electric resistance, a gas transmission coefficient, fuel cell output voltage, and thermal resistance were measured. These results were shown in Table 2.

[0049] The 400g of the same monomer constituents as example of comparison 1 example 1 was put into the glassware of 500mL(s), except the polyolefine system porous membrane (D) of molecular weight 2 million having been immersed for 10 minutes under atmospheric pressure, the same actuation as an example 1 was performed and sulfonic acid type cation exchange membrane was obtained.

[0050] The thickness of such sulfonic acid type cation exchange membrane, cation exchange capacity, electric resistance, a gas transmission coefficient, fuel cell output voltage, and thermal resistance were measured. These results were shown in Table 2.

[0051] Example of comparison 2 polyolefine system porous membrane (A) was immersed in 10% benzene solution of the polystyrene of a mean molecular weight 200,000 for 5 minutes. Then, polyolefine system ***** was taken out out of liquid, and it dried at 50 degrees C. After repeating this actuation 5 times, reduced pressure drying was carried out at 100 degrees C for 2 hours, and the filmy material was obtained.

[0052] The obtained filmy material was immersed for 60 minutes at 40 degrees C into 98% concentrated sulfuric acid, and sulfonic acid type cation exchange membrane was obtained.

[0053] The thickness of such sulfonic acid type cation exchange membrane, cation exchange capacity, electric resistance, a gas transmission coefficient, fuel cell output voltage, and thermal resistance were measured. These results were shown in Table 2.

[0054] Thickness, cation exchange capacity, electric resistance, a gas transmission coefficient, fuel cell output voltage, and thermal resistance were similarly measured using the example of comparison 3 perfluoro KAKABON sulfonic-acid film (commercial item). These results were shown in Table 2.

[0055]
[Table 1]

実施例No.	多孔質膜 ¹⁾	組成			
		S t ²⁾	D V B ³⁾	A T B C ⁴⁾	P O ⁵⁾
1	A	60	40	15	5
2	B	60	40	15	5
3	C	60	40	15	5
4	A	80	20	10	5
5	B	80	20	10	5
6	C	80	20	10	5
比較例 1	D	60	40	15	5

1) 多孔質膜

A ; ポリエチレン製、膜厚 25 μm、空隙率 45%、平均孔径 0.5 μm

B ; ポリエチレン製、膜厚 50 μm、空隙率 60%、平均孔径 0.5 μm

C ; ポリエチレン製、膜厚 25 μm、空隙率 80%、平均孔径 0.5 μm

D ; ポリエチレン製、膜厚 50 μm、空隙率 60%、平均孔径 0.5 μm

2) スチレン

3) ジビニルベンゼン

4) アセチルクエン酸トリプチル

5) t-ブチルパーオキシエチルヘキサノエート

[0056]

[Table 2]

実施例No.	膜厚	イオン 交換容量	含水率	電気抵抗	水素ガス 透過性 × 10 ⁸	酸素ガス 透過性 × 10 ⁸	燃料電池 電圧	耐熱性 収縮率
1	30	1.1	48	0.05	2.5	1.5	0.62	10.3
2	64	1.5	52	0.07	2.2	1.3	0.60	11.5
3	90	2.3	62	0.10	1.9	0.9	0.55	12.8
4	28	1.5	55	0.04	2.8	1.9	0.56	11.4
5	60	2.3	70	0.05	2.4	1.4	0.56	13.4
6	82	2.9	83	0.09	2.1	1.1	0.66	13.6
比較例 1	55	0.4	20	0.40	11.3	9.2	0.32	9.3
比較例 2	30	0.4	15	0.30	20.2	15.2	0.28	10.4
比較例 3	175	0.9	0.9	0.32	3.5	2.4	0.21	12.9

膜厚 [μm]

イオン交換容量 [mmol / g-乾燥膜]

電気抵抗 [Ω · cm²]

含水率 [%]

水素ガス透過性 [cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹]酸素ガス透過性 [cm³ (STP) cm cm⁻² s⁻¹ cmHg⁻¹]

燃料電池出力電圧 [V]

収縮率 [%]

[0057]

[Translation done.]

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TECHNICAL FIELD

[Field of the Invention] This invention relates to the diaphragm for solid-state polyelectrolyte mold fuel cells which consists of a diaphragm for polymer electrolyte fuel cells, and cation exchange membrane which uses polyolefine system porous membrane as a base material in detail.

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PRIOR ART

[Description of the Prior Art] A fuel cell is a generation-of-electrical-energy system which takes out chemical energy when a fuel and an oxidizer are supplied continuously and these react as power. A fuel cell is divided roughly by the class of electrolyte used for this with a phosphoric-acid mold with a comparatively low operating temperature, a solid-state macromolecule mold, the melting carbonate mold that operates at an elevated temperature, and a solid oxide type.

[0003] it be make to act as a fuel cell by join the gas diffusion electrode with which the catalyst be **** (ed) by both sides of the diaphragm of the solid-state macromolecule on which a polymer electrolyte fuel cell act as an electrolyte in these , supply the oxygen content gas which be oxidizers , such as oxygen and air , respectively to ** of the side to which the gas diffusion electrode of another side exist the hydrogen which be a fuel in ** (combustion chamber) of the side in which one gas diffusion electrode exist , and connect an external load circuit between ring main diffusion electrodes .

[0004] The basic structure of such a polymer electrolyte fuel cell is shown in drawing 1 . the inside of drawing, and (1) -- in a cell septum and (2), a combustion chamber side gas diffusion electrode and (5) show an oxidizer room side gas diffusion electrode, and, as for a fuel gas circulation hole and (3), (6) shows the solid-state polyelectrolyte film, as for an oxidizer gas circulation hole and (4). In this polymer electrolyte fuel cell, by the combustion chamber (7), a proton (hydrogen ion) and an electron generate from the supplied hydrogen gas, and this proton conducts the inside of a solid-state polyelectrolyte (6), moves to the oxidizer room (8) of another side, reacts with the oxygen in air or oxygen gas, and generates water. At this time, when the electron generated with the combustion chamber side gas diffusion electrode (4) moves to an oxidizer room side gas diffusion electrode (5) through an external load circuit, electrical energy is obtained.

[0005] In the polymer electrolyte fuel cell of such structure, cation exchange membrane is usually used for the above-mentioned diaphragm. And it is required for this cation exchange membrane small [electric resistance], high [water retention], that gas permeability is low, stable to long-term use, that physical reinforcement should be strong, etc.

[0006] Conventionally, the perfluorocarbon-sulfonic-acid film is mainly used as a cation exchange membrane used as a diaphragm for polymer electrolyte fuel cells. However, although this film was excellent in chemical stability, reduction of the electric resistance by thin-film-izing was [that desiccation of cation exchange membrane arises and the conductivity of a proton tends to fall] difficult for it, since still more nearly physical reinforcement was also inadequate, since water holding capacity was inadequate. Furthermore, the perfluorocarbon-sulfonic-acid film was expensive.

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EFFECT OF THE INVENTION

[Effect of the Invention] Like the above explanation, the diaphragm for solid-state polyelectrolyte mold fuel cells of this invention has low electric resistance, and the cation exchange resin which constructed the bridge over the hole section of polyolefine system porous membrane consists of cation exchange membrane with which it filled up densely without a clearance to details. Therefore, the permeability of gas is very low. Moreover, since polyolefine system porous membrane is a base material, it excels also in dimensional stability or chemical resistance.

[0037] therefore, ** — the crossover of a fuel and an oxidizing agent is controlled and, as for the fuel cell obtained using the diaphragm for solid-state polyelectrolyte mold fuel cells of this invention which has description [like], a high cell output is obtained. And increase of contact resistance with the electrode accompanying swelling contraction is suppressed, and heating sticking by pressure of the gas diffusion electrode can be carried out further there is no adhesive agent in this cation exchange membrane, and good again.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] On the other hand to JP,1-22932,A, as a diaphragm for polymer electrolyte fuel cells The cation exchange membrane with which weight average molecular weight comes to fill up cation exchange resin all over 500,000 or more holes of the polyolefine system porous membrane of the amount of macromolecules is indicated. As the manufacture approach Make a solvent dissolve cation exchange resin in the above-mentioned porous membrane, it is made to sink in, the approach of making a solvent removing, the monomer of cation exchange resin, etc. are infiltrated into the above-mentioned porous membrane after that, and the method of performing the polymerization of the above-mentioned raw material monomer etc. is indicated after that.

[0008] However, when this cation exchange membrane infiltrated into the above-mentioned porous membrane the solution which cation exchange resin dissolves, and its raw material monomer since a base material is the polyolefine of the amount of macromolecules although physical reinforcement was good, this porous membrane did not fully swell it, but it had the problem into which these do not fully enter to the details in a membranous hole. By the approach of infiltrating the solution of cation exchange membrane especially, since a solvent was removed after sinking in, the volume change of packing arose and the restoration nature to the hole section details of the above-mentioned porous membrane was falling further. Moreover, it was difficult to have made it fill up also with the approach of infiltrating a raw material monomer, densely to the hole section details, since these monomers are hyperviscosity in many cases.

[0009] Therefore, the cation exchange membrane obtained by the above-mentioned approach was that from which it does not fill up with cation exchange resin densely to the hole details of a base material, and the permeability of gas is large, therefore it cannot fully suppress that the hydrogen gas of a combustion chamber is spread in an oxidation room side when it is used as said diaphragm for fuel cells, and a big cell output is not obtained. Moreover, ion exchange capacity was low and the electric resistance of ion exchange capacity was also high.

[0010] As mentioned above, it was a big technical problem to have sufficient physical reinforcement and to develop a polymer electrolyte fuel cell diaphragm with low gas permeability small [electric resistance].

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MEANS

[Means for Solving the Problem] this invention persons have continued research wholeheartedly in order to solve the above-mentioned technical problem. Consequently, polyolefine system porous membrane was used as the base material, and electric resistance is small, and it succeeds in gas permeability developing low cation exchange membrane, and came to complete this invention.

[0012] That is, this invention is a diaphragm for solid-state polyelectrolyte mold fuel cells which uses polyolefine system porous membrane as a base material, and it comes to fill up the hole section cation exchange resin, and the electric resistance in a 1 mol/L-sulfuric-acid water solution is two or less 0.20ohm and cm, and is characterized by the transmission coefficient of the hydrogen gas in 50 degrees C consisting of cation exchange membrane which is $3.0 \times 10^{-8} \text{cm}^3$ (STP), $\text{cm} \cdot \text{cm}^{-2}$, s^{-1} , and less than [cmHg^{-1}].

[0013]

[Embodiment of the Invention] As for the cation exchange membrane used in this invention, the free passage hole of polyolefine system porous membrane is filled up with cation exchange resin, and, as for usual, it fills up with the so-called ion exchange resin of a hydrocarbon system completely substantially. That is, the high hydrocarbon system ion exchange resin of the hydration force is the cation exchange membrane of the gestalt distributed to polyolefine system porous membrane, and since the restoration nature of ion exchange resin is high, this cation exchange membrane can be set as the range of a request of electric resistance and the transmission coefficient of hydrogen gas by adjusting ion exchange capacity and fixed ion concentration.

[0014] As polyolefine which is raw material resin of porous membrane, the homopolymer of the alpha olefin of carbon numbers 2-8, other alpha olefins, or a copolymer with other monomers which can be copolymerized is suitably mentioned for ethylene, a propylene, 1-butene, 1-pentene, 1-hexene, a 3-methyl-1-butene, 4-methyl-1-pentene, a 5-methyl-1-heptene, etc. 90% of the weight or more of a thing has the desirable content of the monomer based on an alpha olefin. In such polyolefines, polyethylene and polypropylene are desirable and especially polyethylene is desirable.

[0015] the weight average molecular weight of polyolefine --- 10,000-450,000 --- suitable --- 100,000-450,000 --- 150,000-400,000 are still more suitably desirable. By using the polyolefine of the above-mentioned weight average molecular weight, it becomes possible for porous membrane to become what has low bloating tendency, and for you to make it more densely filled up with this monomer constituent to the hole details in the manufacture approach of the cation exchange membrane mentioned later at the time of sinking [of the monomer constituent for manufacturing cation exchange resin] in.

[0016] In addition, backing according [such polyolefine system porous membrane] to blanket-like objects, such as a product made from polypropylene system fiber, further may be performed.

[0017] 0.1-5 micrometers, suitably, the average aperture of the hole of the above-mentioned polyolefine system porous membrane is 0.1-1 micrometer, and 40 - 90% of thing of voidage is more preferably desirable [an aperture] 30 to 95%. Since electric resistance increases when an average aperture is 0.1 micrometers or less, and a mechanical strength becomes low when an average aperture is 5 micrometers or less, it is not desirable. Moreover, since electric resistance increases when voidage is 30% or less, and a mechanical strength becomes low when voidage is 95% or more, it is not desirable.

[0018] Furthermore, as for polyolefine system porous membrane, what usually has the thickness of 5-100 micrometers from a viewpoint which gives the viewpoint which suppresses electric resistance low, and a mechanical strength required as a supporting lamella is desirable, and what has 10-70 micrometers more preferably is desirable. That to which such polyolefine system porous membrane porosity-ized the polyolefine system film by the extending method etc. is used.

[0019] As for the diaphragm 1 solid-state polyelectrolyte mold fuel cell of this invention, the hole section of the above-mentioned polyolefine system porous membrane is filled up with cation exchange resin. Although it is not limited especially if it is the functional group which can serve as negative charge in the inside of a water solution as a cation-exchange radical of cation exchange resin, a sulfonic group, a carboxylic-acid radical, a phosphonic acid radical, etc. are mentioned, among these, specifically, especially a sulfonic group is desirable.

[0020] Since the thickness of said extent can use thin porous membrane as a base material in the cation exchange membrane used by this invention, the electric resistance in a 1 mol/L-sulfuric-acid water solution is the small value of 0.05–0.15 ohm and cm² suitably two or less 0.20 ohm·cm, and it is advantageous as a diaphragm for cells.

[0021] And since the restoration nature of the cation exchange resin to the hole section of the porous membrane of a base material is high, the permeability of gas is very small [cation exchange membrane], while the cation exchange membrane used by this invention is film with electric resistance small like the above. namely, the transmission coefficient of the hydrogen gas in 50 degrees C — 3.0x10⁻⁸cm³ (STP), cm·cm⁻², s⁻¹, and cmHg⁻¹ it is 0.5–2.0x10⁻⁸cm³ (STP), cm·cm⁻², s⁻¹, and cmHg⁻¹ suitably one or less. Thus, since the transmission coefficient of hydrogen gas is small, that the supplied hydrogen gas penetrates a diaphragm and is spread in oxygen gas can prevent the diaphragm for solid-state polyelectrolyte mold fuel cells of this invention which consists of this cation exchange membrane good, and the cell of a high output is obtained.

[0022] In addition, generally the cation exchange membrane used by this invention which has the transmission coefficient of the above-mentioned hydrogen gas has the value of 2.0x10⁻⁸cm³ (STP), cm·cm⁻², s⁻¹ and less than [cmHg⁻¹], and also 0.3–1.5x10⁻⁸cm³ (STP), cm·cm⁻², s⁻¹ and cmHg⁻¹ as a transmission coefficient of the oxygen gas in 50 degrees C. Therefore, transparency of the diaphragm of oxygen gas can also prevent the polymer electrolyte fuel cell diaphragm of this invention good.

[0023] Furthermore, as for the cation exchange membrane used by this invention, it is desirable that the viewpoint which maintains electric resistance at the above-mentioned range to cation exchange capacity is 0.5 – 3.0 mmol/g suitably 0.2 to 5.0 mmol/g.

[0024] Moreover, as for water content, it is suitably desirable that it is 40% or more 30% or more so that it may be hard to produce the conductive fall of the proton by desiccation. Generally water content is held at about 30 – 90%. In order to obtain the water content of such range, it is controllable by the class, the cation exchange capacity, and the degree of cross linking of the cation exchange resin which exists in the hole section of porous membrane.

[0025] Although the cation exchange membrane which has such description may be manufactured by what kind of approach, generally it is manufactured by the following approaches. That is, after making it sink in, carrying out reduced pressure deaeration of the monomer constituent which consists of the monomer, cross-linking monomer, and polymerization initiator which have the functional group or cation-exchange radical which can introduce a cation-exchange radical at polyolefine system porous membrane, the polymerization of the monomer constituent is carried out and the approach of introducing a cation-exchange radical if needed is mentioned.

[0026] It is used in this manufacture approach, without limiting especially the hydrocarbon system monomer used in manufacture of conventionally well-known cation exchange resin as a monomer which has the monomer or cation-exchange radical which has the functional group which can introduce cation exchange membrane. Specifically as a monomer which has the functional group which can introduce a cation-exchange radical, styrene, vinyltoluene, a vinyl xylene, alpha methyl styrene, vinyl naphthalene, alpha-halogenation styrene, etc. are mentioned. Moreover, as a monomer which has a cation-exchange radical, phosphonic acid system monomers, such as carboxylic-acid system monomers, such as sulfonic-acid system monomers, such as a styrene sulfonic acid, a vinyl sulfonic acid, and alpha-halogenation vinyl sulfonic acid, a methacrylic acid, an acrylic acid, and a maleic anhydride, and a vinyl phosphoric acid, those salts, and ester are used.

[0027] Moreover, especially as a cross-linking monomer, although not restricted, divinyl compounds, such as divinylbenzenes, a divinyl sulfone, a butadiene, a chloroprene, divinylbiphenyl, trivinylbenzene, divinyl naphthalene, a diaryl amine, and a divinyl pyridine, are used, for example.

[0028] In this invention, these monomers, other monomers which can be copolymerized, and plasticizers other than the monomer which has the monomer or cation-exchange radical which has the functional group which can introduce the above-mentioned cation-exchange radical, or a cross-linking monomer may be added if needed. As other monomers carried out like this, styrene, acrylonitrile, methyl styrene, an acrolein, a methyl vinyl ketone, a vinyl biphenyl, etc. are used, for example. Moreover, as plasticizers, dibutyl

phthalate, dioctyl phthalate, c. ethyl isophthalate, a dibutyl horse ma. erel peat, triethyl SHITORETO, acetyl tributyl citrate, dibutyl sebacate, etc. are used.

[0029] Next, as a polymerization initiator in this invention, a well-known thing is conventionally used especially without a limit. As an example of such a polymerization initiator, organic peroxide, such as octanoyl peroxide, lauroyl peroxide, t-butylperoxy2-ethylhexanoate, benzoyl peroxide, t-buthylperoxy isobutyrate, t-butyl peroxy laurate, t-hexyl peroxy benzoate, and G t-butyl peroxide, is used.

[0030] In this invention, the blending ratio of coal of each component which constitutes a monomer constituent In order to attain the purpose of this invention, generally As opposed to the monomer 100 weight section which has the monomer or cation-exchange radical which has the functional group which can introduce a cation-exchange radical It is suitable to carry out 0-50 weight section use of the cross-linking monomer to the above-mentioned monomer, when adding the 0 - 100 weight section and plasticizers for 1 - 40 weight section, and these monomers and other monomers which can be copolymerized suitably, 0.1 - 50 weight section and. Moreover, it is desirable 0.1 - 20 weight section and to carry out 0.5-10 weight section combination of the polymerization initiator suitably to the monomer 100 weight section which has the monomer or cation-exchange radical which has the functional group which can introduce a cation-exchange radical.

[0031] Especially the restoration approach of the above-mentioned monomer constituent to the polyolefine system porous membrane which is a base material is not limited. For example, what is necessary is just to make it sink in, carrying out reduced pressure deaeration of the monomer group living thing at polyolefine system porous membrane. If it deaerates and infiltrates filling up high density with the above-mentioned monomer constituent to the details of the hole section of polyolefine system porous membrane under reduced pressure in this way to being difficult, it will become possible to be filled up with a monomer constituent without a clearance to these hole section details, as described above. And the cation exchange membrane obtained by carrying out the polymerization of the monomer constituent turns into film with very low gas permeability which said invention in this application specifies after this sinking in.

[0032] Here, sinking-in processing while [above-mentioned] carrying out reduced pressure deaeration is contacted under the reduced pressure to polyolefine system porous membrane of a monomer constituent, and, specifically, is performed by returning a pressure to atmospheric pressure. For example, polyolefine system porous membrane is immersed in the monomer mixture which put the monomer constituent into the method of introducing into a container and infiltrating it until it returns to atmospheric pressure, or the container after putting polyolefine system porous membrane into the container and changing into a reduced pressure condition with a vacuum pump, and after carrying out reduced pressure deaeration of the gas in a hole with a vacuum pump, the approach of returning to atmospheric pressure is mentioned. Whenever [reduced pressure / when decompressing] has a desirable pressure until a monomer boils under 7kPa - working temperature, and it is desirable to choose from the range of 2kPa-0.1kPa especially. What is necessary is for the temperature at the time of sinking in to have common 20 degrees C or less, and just to usually choose sinking-in time amount suitably in the range for 5 - 60 minutes.

[0033] In order to postpolymerize, the approach of inserting into films, such as polyester, generally and carrying out a temperature up from ordinary temperature under pressurization which the above-mentioned polyolefine system porous membrane was made to fill up with a monomer constituent is desirable. What is necessary is for such polymerization conditions not to be influenced by the presentation of the class of polymerization initiator which involves, and a monomer constituent etc., not to limit them by the way, and just to choose them suitably.

[0034] The filmy material which a polymerization is carried out as mentioned above and obtained can introduce the cation-exchange radical of a request of this by processing of well-known sulfonation, the Krol sulfonation, phosphonium-izing, hydrolysis, etc. if needed, and can use it as cation exchange membrane.

[0035] this invention -- setting -- the above -- a well-known structure thing can apply the solid oxide fuel cell for which the cation exchange membrane of description is used as a diaphragm that there is no limit in any way. Usually, it is common to be applied to what has structure as shown in above mentioned drawing 1.

[Translation done.]

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EXAMPLE

[Example] Although an example and the example of a comparison are hereafter hung up and explained in order to explain this invention still more concretely, this invention is not limited to these examples.

[0039] In addition, the property of the cation exchange membrane shown in an example and the example of a comparison shows the value measured by the following approaches.

(1) Cation exchange capacity;

After being immersed in 1 mol/L-HCl for 10 hours or more and using cation exchange membrane as a hydrogen ion mold, the quantum of the hydrogen ion which was made to permute by the sodium ion mold and separated by 1 mol/L-NaCl was carried out with potentiometric titration equipment (COMTITE-900, Hiranuma Sangyo Co., Ltd. make) (Amol).

[0040] Next, reduced pressure drying of the same cation exchange membrane was carried out at 60 degrees C for 5 hours, and the weight was measured (Wg). Cation exchange capacity was calculated by the degree type.

Cation exchange capacity = Ax1000/W [the mmol/g-desiccation film]

(2) Cation exchange membrane was placed in the center of the two-room cel equipped with the electric resistance platinum electrode, and 25-degree C 3 mol/L sulfuric-acid water solution was filled in the cel. The Luggin capillary was prepared in the both sides of cation exchange membrane, and liquid junction was carried out to the reference electrode with the salt bridge. The potential (bV) when passing the current of 100 mA/cm², without inserting the potential (aV) and the film when passing the current of 100 mA/cm² on both sides of the film was measured. The electric resistance of cation exchange membrane was searched for from the degree type.

[0041]

Electric resistance = 1000x (a-b)/100 [omegam²]

(3) After having been immersed in 1 mol/L-HCl for 4 hours or more, using water content cation exchange membrane as the hydrogen ion mold and fully rinsing it with ion exchange water, the film was taken out, surface moisture was wiped off by KIMUWAIPU etc., and the weight at the time of humidity (Wg) was measured. Next, reduced pressure drying of the film was carried out at 60 degrees C for 5 hours, and the weight at the time of desiccation (Dg) was measured. It asked for the water content of cation exchange membrane by the degree type.

[0042]

Water content = 1000x (W-D) / D [%]

(4) As a measuring method of a gas transmission coefficient gas transmission coefficient, the gas radiographic examination machine by the U-tube-construction mercury manometer (based on JIS Z 1707) was used. In 50 degrees C, the gas radiographic examination machine was equipped with the cation exchange membrane used for measurement by the moisture state. Moreover, the oxygen or hydrogen maintained at saturation temperature in 50 degrees C was used for the gas used for measurement. It asked for the gas transmission coefficient by the degree type.

[0043]

$$P=(p/t)x(1/A) \times [1/(Pa-Pb)]$$

P: Gas transmission coefficient (cm³ (STP), cm⁻², s⁻¹, and cmHg⁻¹)

p: The amount of gas transparency (cm³ (STP))

t: measuring time (s)

l: Cation-exchange-membrane thickness (cm)

A: Gas transparency area (cm²)

Pa: High-tension-side gas pressure (cmHg)

Pb: Low-tension side gas pressure (cmHg)

(5) On carbon paper of 80% of void contents which carried out water-repellent treatment by fuel cell output voltage polytetrafluoroethylene, what mixed 5% solution (the Du Pont make, trade name NAFION) of water with the carbon black of *** of 30 % of the weight of platinum and the alcohol of perfluorocarbon sulfonic acid was applied, reduced pressure drying was carried out at 80 degrees C for 4 hours, and it considered as the gas diffusion electrode.

[0044] Next, after setting the above-mentioned gas diffusion electrode to both sides of the cation exchange membrane to measure and carrying out a heat press for 100 seconds under 150 degrees C and pressurization with a pressure of 100kg/cm², it was left for 2 minutes at the room temperature. It included in the fuel cell cel which shows this to drawing 1, and the output voltage at the time of 200 mL/min and 400 mL/min was measured for oxygen with pressure 2 atmospheric pressure, a fuel cell cel temperature [of 50 degrees C], and a humidification temperature of 50 degrees C, and hydrogen, respectively.

(6) Thermal resistance (contraction)

After leaving the sample film for measurement which carried out predrying in the 50-degree C dryer for 1 hour in a 160-degree C dryer for 30 minutes, it took out from the dryer, the dimension was measured and contraction was searched for by the following formulas.

[0045] S=100x (La-Lb)/LaS: Contraction (%)

La: The die length of the film dried in the 50 degree C dryer (cm)

Lb: The die length of the film left in the 160 degree C dryer for 30 minutes (cm)

According to the presentation table having shown in one to example 6 table 1, various monomers etc. were mixed and the monomer constituent was obtained. 400g of obtained monomer constituents was put into the glassware of 500mL(s), and the polyolefine system porous membrane (A, B, C, every 20cmx 20cm) of weight average molecular weight 350,000 was immersed.

[0046] Next, glassware was made reduced pressure for 10 minutes to the pressure of 0.7kPa(s) with the vacuum pump, after carrying out reduced pressure deaeration, it returned to ordinary pressure and the hole of polyolefine system porous membrane was filled up with the monomer constituent. Then, polyolefine system porous membrane was taken out out of the monomer constituent, and after covering the both sides of polyolefine system porous membrane by making 100-micrometer polyester film into a remover, the heating polymerization was carried out under 3kg/cm² nitrogen pressurization for 80-degree-C 5 hours.

[0047] The obtained filmy material was immersed for 45 minutes at 40 degrees C into the 1:1 mixture of 98% concentrated sulfuric acid and the chlorosulfonic acid of 90% or more of purity, and sulfonic acid type cation exchange membrane was obtained.

[0048] The thickness of such sulfonic acid type cation exchange membrane, cation exchange capacity, electric resistance, a gas transmission coefficient, fuel cell output voltage, and thermal resistance were measured. These results were shown in Table 2.

[0049] The 400g of the same monomer constituents as example of comparison 1 example 1 was put into the glassware of 500mL(s), except the polyolefine system porous membrane (D) of molecular weight 2 million having been immersed for 10 minutes under atmospheric pressure, the same actuation as an example 1 was performed and sulfonic acid type cation exchange membrane was obtained.

[0050] The thickness of such sulfonic acid type cation exchange membrane, cation exchange capacity, electric resistance, a gas transmission coefficient, fuel cell output voltage, and thermal resistance were measured. These results were shown in Table 2.

[0051] Example of comparison 2 polyolefine system porous membrane (A) was immersed in 10% benzene solution of the polystyrene of a mean molecular weight 200,000 for 5 minutes. Then, polyolefine system ***** was taken out out of liquid, and it dried at 50 degrees C. After repeating this actuation 5 times, reduced pressure drying was carried out at 100 degrees C for 2 hours, and the filmy material was obtained.

[0052] The obtained filmy material was immersed for 60 minutes at 40 degrees C into 98% concentrated sulfuric acid, and sulfonic acid type cation exchange membrane was obtained.

[0053] The thickness of such sulfonic acid type cation exchange membrane, cation exchange capacity, electric resistance, a gas transmission coefficient, fuel cell output voltage, and thermal resistance were measured. These results were shown in Table 2.

[0054] Thickness, cation exchange capacity, electric resistance, a gas transmission coefficient, fuel cell output voltage, and thermal resistance were similarly measured using the example of comparison 3 perfluoro KAKABON sulfonic-acid film (commercial item). These results were shown in Table 2.

[0055]

[Table 1]

実施例No.	多孔質膜 ¹⁾	組成			
		S t ²⁾	D V B ³⁾	A T B C ⁴⁾	P O ⁵⁾
1	A	60	40	15	5
2	B	60	40	15	5
3	C	60	40	15	5
4	A	80	20	10	5
5	B	80	20	10	5
6	C	80	20	10	5
比較例1	D	60	40	15	5

1) 多孔質膜

A ; ポリエチレン製、膜厚25 μm、空隙率45%、平均孔径0.5 μm

B ; ポリエチレン製、膜厚50 μm、空隙率60%、平均孔径0.5 μm

C ; ポリエチレン製、膜厚25 μm、空隙率80%、平均孔径0.5 μm

D ; ポリエチレン製、膜厚50 μm、空隙率60%、平均孔径0.5 μm

2) スチレン

3) ジビニルベンゼン

4) アセチルクエン酸トリプチル

5) t-ブチルパーオキシエチルヘキサノエート

[0056]

[Table 2]

実施例No.	膜厚	イオン 交換容量	含水率	電気抵抗	水素ガス 透過性×10 ⁸	酸素ガス 透過性×10 ⁸	燃料電池 電圧	耐熱性 収縮率
1	30	1.1	48	0.06	2.6	1.5	0.62	10.3
2	64	1.5	52	0.07	2.2	1.3	0.60	11.5
3	90	2.3	62	0.10	1.9	0.9	0.66	12.8
4	28	1.5	55	0.04	2.8	1.9	0.56	11.4
5	60	2.3	70	0.05	2.4	1.4	0.56	13.4
6	82	2.9	83	0.09	2.1	1.1	0.66	13.6
比較例1	55	0.4	20	0.40	11.3	9.2	0.32	9.3
比較例2	30	0.4	15	0.30	20.2	15.2	0.28	10.4
比較例3	175	0.9	0.9	0.32	3.5	2.4	0.21	12.9

膜厚[μm]

イオン交換容量[mmol/g-乾燥膜]

電気抵抗[Ω·cm²]

含水率[%]

水素ガス透過性[c m³ (S T P) c m c m⁻² s⁻¹ c m H g⁻¹]酸素ガス透過性[c m³ (S T P) c m c m⁻² s⁻¹ c m H g⁻¹]

燃料電池出力電圧[V]

収縮率[%]

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] Drawing 1 is the conceptual diagram showing the basic structure of a solid-state polyelectrolyte mold fuel cell.

[Description of Notations]

- 1; cell septum
- 2; fuel gas circulation hole
- 3; oxidizer gas circulation hole
- 4; combustion chamber side gas diffusion electrode
- 5; oxidizer room side gas diffusion electrode
- 6; solid-state polyelectrolyte
- 7; combustion chamber
- 8; oxidizer room

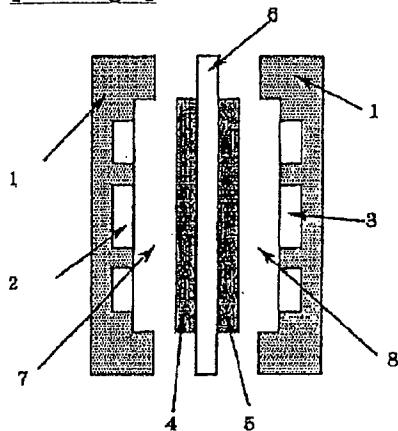
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DRAWINGS

[Drawing 1]

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(54)【発明の名称】 固体高分子電解質型燃料電池用隔膜

(57)【要約】

【課題】十分な物理的強度を有し、電気抵抗が小さく、且つガス透過性が低い、固体高分子型燃料電池隔膜を開発すること。

【解決手段】ポリオレフィン系多孔質膜、好適には重量平均分子量が10万～45万であるポリオレフィン系多孔質膜母材とし、その空孔部に陽イオン交換樹脂が充填されてなり、1mol/L-硫酸水溶液中の電気抵抗が0.20Ω・cm²以下であり、50℃における水素ガスの透過係数が3.0×10⁻⁸cm³(S T P)・cm²・cmHg⁻¹以下である陽イオン交換膜からなることを特徴とする固体高分子電解質型燃料電池用隔膜。

【特許請求の範囲】

【請求項1】ポリオレフィン系多孔質膜を母材とし、その空孔部に陽イオン交換樹脂が充填されてなり、 $1 \text{ m} \cdot 1/\text{L} \cdot \text{硫酸水溶液}$ 中の電気抵抗が $0.20 \Omega \cdot \text{cm}^2$ 以下であり、 50°C における水素ガスの透過係数が $3.0 \times 10^{-8} \text{ cm}^3 (\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$ 以下である陽イオン交換膜からなることを特徴とする固体高分子電解質型燃料電池用隔膜。

【請求項2】ポリオレフィン系多孔質膜の重量平均分子量が、10万～45万である請求項1記載の固体高分子電解質型燃料電池用隔膜。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、固体高分子型燃料電池用隔膜、詳しくはポリオレフィン系多孔質膜を母材とする陽イオン交換膜からなる固体高分子電解質型燃料電池用隔膜に関する。

【0002】

【従来の技術】燃料電池は、燃料と酸化剤とを連続的に供給し、これらが反応した時の化学エネルギーを電力として取り出す発電システムである。燃料電池は、これに用いる電解質の種類によって、動作温度が比較的低いリン酸型、固体高分子型、高温で動作する溶融炭酸塩型、固体電解質型と大別される。

【0003】これらの中で、固体高分子型燃料電池は、電解質として作用する固体高分子の隔膜の両面に触媒が担持されたガス拡散電極を接合し、一方のガス拡散電極が存在する側の室（燃料室）に燃料である水素を、他方のガス拡散電極が存在する側の室に酸化剤である酸素や空気等の酸素含有ガスをそれぞれ供給し、両ガス拡散電極間に外部負荷回路を接続することにより、燃料電池として作用させる。

【0004】こうした固体高分子型燃料電池の基本構造を図1に示す。図中、（1）は電池隔壁、（2）は燃料ガス流通孔、（3）は酸化剤ガス流通孔、（4）は燃料室側ガス拡散電極、（5）は酸化剤室側ガス拡散電極、（6）は固体高分子電解質膜を示す。この固体高分子型燃料電池において、燃料室（7）では、供給された水素ガスからプロトン（水素イオン）と電子が生成し、このプロトンは固体高分子電解質（6）内を伝導し、他方の酸化剤室（8）に移動し、空気又は酸素ガス中の酸素と反応して水を生成する。この時、燃料室側ガス拡散電極（4）で生成した電子は、外部負荷回路を通じて酸化剤室側ガス拡散電極（5）へと移動することにより電気エネルギーが得られる。

【0005】このような構造の固体高分子型燃料電池において、上記隔膜には、通常、陽イオン交換膜が使用される。そして、この陽イオン交換膜には、電気抵抗が小さいこと、保水性が高いこと、ガス透過性が低いこと、長期の使用に対して安定であること、物理的な強度が強

いことなどが要求される。

【0006】従来、固体高分子型燃料電池用隔膜として使用される陽イオン交換膜として、パーカルオロカーボンスルホン酸膜が主に使用されている。しかし、この膜は、化学的安定性に優れているが、保水力が不十分であるため陽イオン交換膜の乾燥が生じてプロトンの伝導性が低下し易く、さらに物理的な強度も不十分であるために薄膜化による電気抵抗の低減が困難であった。更にパーカルオロカーボンスルホン酸膜は高価であった。

【0007】

【発明が解決しようとする課題】一方、特開平1-22932号公報には、固体高分子型燃料電池用隔膜として、重量平均分子量が50万以上の高分子量のポリオレフィン系多孔質膜の空孔中に陽イオン交換樹脂を充填してなる陽イオン交換膜が開示され、その製造方法として、上記多孔質膜に、陽イオン交換樹脂を溶剤に溶解させて含浸させ、その後、溶剤を除去させる方法や、陽イオン交換樹脂の単量体等を上記多孔質膜に含浸させ、その後、上記原料単量体の重合を行う方法などが開示されている。

【0008】しかしながら、この陽イオン交換膜は、物理的強度は良好であるものの、母材が高分子量のポリオレフィンであるため、陽イオン交換樹脂が溶解する溶液やその原料単量体を上記多孔質膜に含浸させる際に、該多孔質膜が十分に膨潤せず、これらが膜の空孔内の細部まで充分に入り込まない問題があった。特に、陽イオン交換膜の溶液を含浸させる方法では、含浸後に溶剤が除去されるため、充填物の体積変化が生じてしまい、上記多孔質膜の空孔部細部への充填性はさらに低下していた。また、原料単量体を含浸させる方法でも、これらの単量体は多くの場合高粘度であるため、その空孔部細部まで密に充填することは困難であった。

【0009】従って、上記方法で得られる陽イオン交換膜は、母材の空孔細部まで密に陽イオン交換樹脂が充填されていないものであり、そのためガスの透過性が大きく、前記燃料電池用隔膜として使用した際には、燃料室の水素ガスが酸化室側に拡散することを十分に抑えることが出来ず、大きな電池出力が得られないものであった。また、イオン交換容量が低くかつ電気抵抗も高いものであった。

【0010】以上から、十分な物理的強度を有し、電気抵抗が小さく、且つガス透過性が低い、固体高分子型燃料電池隔膜を開発することが大きな課題であった。

【0011】

【課題を解決するための手段】本発明者らは、上記課題を解決するため鋭意研究を続けてきた。その結果、ポリオレフィン系多孔質膜を母材とし、電気抵抗が小さく、ガス透過性が低い陽イオン交換膜を開発することに成功し、本発明を完成するに至った。

【0012】即ち、本発明は、ポリオレフィン系多孔質

膜を母材とし、その空孔部に陽イオン交換樹脂が充填されてなり、 1 mol/L -硫酸水溶液中の電気抵抗が $0.20\Omega \cdot \text{cm}^2$ 以下であり、 50°C における水素ガスの透過係数が $3.0 \times 10^{-8}\text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$ 以下である陽イオン交換膜からなることを特徴とする固体高分子電解質型燃料電池用隔膜である。

【0013】

【発明の実施の形態】本発明において使用する陽イオン交換膜は、ポリオレフィン系多孔質膜の連通孔に実質的に完全に陽イオン交換樹脂、通常は、いわゆる炭化水素系のイオン交換樹脂が充填されている。即ち、水和力の高い炭化水素系イオン交換樹脂がポリオレフィン系多孔質膜に分散した形態の陽イオン交換膜であり、イオン交換樹脂の充填性が高いため、該陽イオン交換膜は、イオン交換容量や固定イオン濃度を調整することにより、電気抵抗や水素ガスの透過係数を所望の範囲に設定することが出来る。

【0014】多孔質膜の原料樹脂であるポリオレフィンとしては、エチレン、プロピレン、1-ブテン、1-ペンテン、1-ヘキセン、3-メチル-1-ブテン、4-メチル-1-ペンテン、5-メチル-1-ヘプテン等の好適には炭素数2~8の α -オレフィンの単独重合体、または他の α -オレフィン或いは共重合可能な他の単量体との共重合体が挙げられる。 α -オレフィンに基づく単量体の含有量が90重量%以上のものが好ましい。これらのポリオレフィンにおいて、ポリエチレン、ポリプロピレンが好ましく、特にポリエチレンが好ましい。

【0015】ポリオレフィンの重量平均分子量は、1万~45万、好適には10万~45万、さらに好適には15~40万が好ましい。上記重量平均分子量のポリオレフィンを用いることにより、多孔質膜は膨潤性が低いものになり、後述する陽イオン交換膜の製造方法において、陽イオン交換樹脂を製造するための単量体組成物の含浸時に、その空孔細部までより密に該単量体組成物を充填させることが可能になる。

【0016】なお、これらのポリオレフィン系多孔質膜は、更に、ポリプロピレン系繊維製等の布状物によるパンキングが施されていても良い。

【0017】上記ポリオレフィン系多孔質膜の孔の平均孔径は $0.1\sim 5\mu\text{m}$ 、好適には $0.1\sim 1\mu\text{m}$ であり、空隙率が30~95%、より好ましくは40~90%のものが好ましい。平均孔径が $0.1\mu\text{m}$ 以下の場合には電気抵抗が増大し、平均孔径が $5\mu\text{m}$ 以下の場合には、機械的強度が低くなるので好ましくない。また、空隙率が30%以下の場合には電気抵抗が増大し、空隙率が95%以上の場合には機械的強度が低くなるので好ましくない。

【0018】さらに、ポリオレフィン系多孔質膜は、電気抵抗を低く抑える観点及び支持膜として必要な機械的

強度を付与する観点から、通常 $5\sim 100\mu\text{m}$ の厚みを有するものが好ましく、より好ましくは $10\sim 70\mu\text{m}$ を有するものが好ましい。これらのポリオレフィン系多孔質膜は、ポリオレフィン系フィルムを延伸法等により、多孔質化したものが使用される。

【0019】本発明の固体高分子電解質型燃料電池用隔膜は、上記ポリオレフィン系多孔質膜の空孔部に陽イオン交換樹脂が充填されたものである。陽イオン交換基としては、水溶液中での負の電荷となりうる官能基なら特に限定されるものではないが、具体的には、スルホン酸基、カルボン酸基、ホスホン酸基等が挙げられ、このうちスルホン酸基が特に好ましい。

【0020】本発明で使用する陽イオン交換膜では、前記程度の膜厚が薄い多孔質膜を母材として用いることが出来るため、 1 mol/L -硫酸水溶液中の電気抵抗が $0.20\Omega \cdot \text{cm}^2$ 以下好適には $0.05\sim 0.15\Omega \cdot \text{cm}^2$ の小さい値であり、電池用隔膜として有利である。

【0021】そして、本発明で使用する陽イオン交換膜は、上記の如く電気抵抗が小さい膜であると共に、母材の多孔質膜の空孔部への陽イオン交換樹脂の充填性が高いため、ガスの透過性が極めて小さい。即ち、 50°C における水素ガスの透過係数が $3.0 \times 10^{-8}\text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$ 以下、好適には $0.5\sim 2.0 \times 10^{-8}\text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$ である。このように水素ガスの透過係数が小さいため、該陽イオン交換膜からなる本発明の固体高分子電解質型燃料電池用隔膜は、供給した水素ガスが隔膜を透過して酸素ガス中に拡散することが良好に防止でき、高い出力の電池が得られる。

【0022】なお、上記水素ガスの透過係数を有する本発明で使用する陽イオン交換膜は、 50°C における酸素ガスの透過係数としては、一般に $2.0 \times 10^{-8}\text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$ 以下、更には $0.3\sim 1.5 \times 10^{-8}\text{ cm}^3(\text{STP}) \cdot \text{cm} \cdot \text{cm}^{-2} \cdot \text{s}^{-1} \cdot \text{cmHg}^{-1}$ の値を有している。従って、本発明の固体高分子型燃料電池隔膜は、酸素ガスの隔膜の透過も良好に防止できる。

【0023】さらに、本発明で使用する陽イオン交換膜は、電気抵抗を上記範囲に保つ観点から、陽イオン交換容量が $0.2\sim 5.0\text{ mmol/g}$ 、好適には、 $0.5\sim 3.0\text{ mmol/g}$ であるのが好ましい。

【0024】また、乾燥によるプロトンの伝導性の低下が生じ難いように、含水率は、30%以上、好適には40%以上であるのが好ましい。一般には含水率は30~90%程度で保持される。このような範囲の含水率を得るために、多孔質膜の空孔部に存在する陽イオン交換樹脂の種類、陽イオン交換容量及び架橋度により制御することが出来る。

【0025】このような性状を有する陽イオン交換膜

は、如何なる方法により製造しても良いが、一般には、以下の方法により製造される。即ち、陽イオン交換基が導入可能な官能基または陽イオン交換基を有する単量体、架橋性単量体および重合開始剤からなる単量体組成物をポリオレフィン系多孔質膜に減圧脱気しながら含浸させた後、単量体組成物を重合し、必要に応じて陽イオン交換基を導入する方法が挙げられる。

【0026】この製造方法において、陽イオン交換膜が導入可能な官能基を有する単量体または陽イオン交換基を有する単量体としては、従来公知である陽イオン交換樹脂の製造において用いられている炭化水素系単量体が特に限定されずに使用される。具体的には、陽イオン交換基が導入可能な官能基を有する単量体としては、ステレン、ビニルトルエン、ビニルキシレン、 α -メチルスチレン、ビニルナフタレン、 α -ハロゲン化スチレン等が挙げられる。また、陽イオン交換基を有する単量体としては、ステレンスルホン酸、ビニルスルホン酸、 α -ハロゲン化ビニルスルホン酸等のスルホン酸系単量体、メタクリル酸、アクリル酸、無水マレイン酸等のカルボン酸系単量体、ビニルリン酸等のホスホン酸系単量体、それらの塩およびエステル類等が用いられる。

【0027】また、架橋性単量体としては、特に制限されるものではないが、例えば、ジビニルベンゼン類、ジビニルスルホン、ブタジエン、クロロブレン、ジビニルビフェニル、トリビニルベンゼン類、ジビニルナフタレン、ジアリルアミン、ジビニルビリジン等のジビニル化合物が用いられる。

【0028】本発明では、上記した陽イオン交換基が導入可能な官能基を有する単量体または陽イオン交換基を有する単量体や架橋性単量体の他に、必要に応じてこれらの単量体と共に重合可能な他の単量体や可塑剤類を添加しても良い。こうした他の単量体としては、例えば、ステレン、アクリロニトリル、メチルスチレン、アクリレイン、メチルビニルケトン、ビニルビフェニル等が用いられる。また、可塑剤類としては、ジブチルタレート、ジオクチルタレート、ジメチルイソフタレート、ジブチルアジペート、トリエチルシトレート、アセチルトリブチルシトレート、ジブチルセバケート等が用いられる。

【0029】次に、本発明における重合開始剤としては、従来公知のものが特に制限なく使用される。こうした重合開始剤の具体例としては、オクタノイルパーオキシド、テウロイルパーオキシド、 t -ブチルパーオキシ-2-エチルヘキサノエート、ベンゾイルパーオキシド、 t -ブチルパーオキシソブチレート、 t -ブチルパーオキシラウレート、 t -ヘキシリパーオキシベンゾエート、ジー t -ブチルパーオキシド等の有機過酸化物が用いられる。

【0030】本発明において、単量体組成物を構成する各成分の配合割合は、本発明の目的を達成するために

は、一般には、陽イオン交換基が導入可能な官能基を有する単量体または陽イオン交換基を有する単量体100重量部に対して、架橋性単量体を0.1～50重量部、好適には1～40重量部、これらの単量体と共に重合可能な他の単量体を0～100重量部、可塑剤類を添加する場合は上記単量体に対して0～50重量部使用するのが好適である。また、重合開始剤は、陽イオン交換基が導入可能な官能基を有する単量体または陽イオン交換基を有する単量体100重量部に対して、0.1～20重量部、好適には0.5～10重量部配合させるのが好ましい。

【0031】母材であるポリオレフィン系多孔質膜への上記単量体組成物の充填方法は、特に限定されない。例えば、単量体組成物をポリオレフィン系多孔質膜に、減圧脱気しながら含浸させれば良い。前記したとおり、ポリオレフィン系多孔質膜の空孔部の細部まで上記単量体組成物を高密度に充填することは困難であるのに対して、このように減圧下で脱気して含浸させれば、該空孔部細部まで隙間なく単量体組成物を充填することが可能になる。そしてかかる含浸後、単量体組成物を重合することで得られる陽イオン交換膜は、前記本願発明が特定するようなガス透過性が極めて低い膜になる。

【0032】ここで、上記減圧脱気しながらの含浸処理は、具体的には、単量体組成物をポリオレフィン系多孔質膜に減圧下で接触させ、圧力を大気圧に戻すことで行われる。例えば、ポリオレフィン系多孔質膜を容器に入れ、真空ポンプで減圧状態にした後、単量体組成物を大気圧に戻すまで容器に導入して含浸させる方法、または、容器に入れた単量体混合物にポリオレフィン系多孔質膜を浸漬し、真空ポンプで孔中の気体を減圧脱気した後大気圧に戻す方法が挙げられる。減圧する時の減圧度は、7 kPa～作業温度下で単量体が沸騰するまでの圧力が好ましく、特に2 kPa～0.1 kPaの範囲から選択するのが好ましい。含浸時の温度は、20℃以下が一般的であり、含浸時間は、通常、5～60分の範囲で適宜選択すれば良い。

【0033】単量体組成物を上記ポリオレフィン系多孔質膜に充填させた後重合するには、一般にポリエステル等のフィルムに挟んで加圧下で常温から昇温する方法が好ましい。こうした重合条件は、関与する重合開始剤の種類、単量体組成物の組成等によって左右されるものであり、時に限定されるものではなく適宜選択すれば良い。

【0034】以上のように重合されて得られる膜状物は、必要に応じてこれを、公知の例ええばスルホン化、クロルスルホン化、ホスホニウム化、加水分解等の処理により所望の陽イオン交換基を導入して、陽イオン交換膜と/orすることができる。

【0035】本発明において、上記性状の陽イオン交換膜が隔膜として使用される固体電解質型燃料電池は、公

知の構造ものが何ら制限なく適用できる。通常は、前記した図1に示されるような構造をしたものに適用されるのが一般的である。

【0036】

【発明の効果】以上の説明の如く本発明の固体高分子電解質型燃料電池用隔膜は、電気抵抗が低く、ポリオレフィン系多孔質膜の空孔部に架橋した陽イオン交換樹脂が細部まで隙間なく密に充填された陽イオン交換膜からなる。従って、ガスの透過性が極めて低い。また、ポリオレフィン系多孔質膜が母材であることから、寸法安定性や耐薬品性にも優れている。

【0037】従って、かのような性状を有する本発明の固体高分子電解質型燃料電池用隔膜を使用して得られる燃料電池は、燃料および酸化剤のクロスオーバーが抑制されて高い電池出力が得られるものになる。そしてまた、膨潤収縮に伴う電極との接触抵抗の増大が抑えられ、さらには、ガス拡散電極を該陽イオン交換膜に接着不良なく良好に加熱圧着できるものになる。

【0038】

【実施例】本発明を更に具体的に説明するため、以下、実施例及び比較例を掲げて説明するが、本発明はこれらの実施例に限定されるものではない。

【0039】なお、実施例および比較例に示す陽イオン交換膜の特性は、以下の方法により測定した値を示す。

(1) 陽イオン交換容量：

陽イオン交換膜を1mol/L-HClに10時間以上浸漬し、水素イオン型とした後、1mol/L-NaClでナトリウムイオン型に置換させ遊離した水素イオンを電位差滴定装置(COMTITE-900、平沼産業株式会社製)で定量した(Amol)。

【0040】次に、同じ陽イオン交換膜を60°Cで5時間減圧乾燥させその重量を測定した(Wg)。陽イオン交換容量は次式により求めた。

$$\text{陽イオン交換容量} = A \times 1000 / W \quad [\text{mmol/g - 乾燥膜}]$$

(2) 電気抵抗

白金電極を備えた2室セルの中央に陽イオン交換膜を置き、セル内に25°Cの3mol/L硫酸水溶液を満たした。陽イオン交換膜の両側にはルギン管を設け、塩橋により参照電極と液絡した。膜を挟んで100mA/cm²の電流を流したときの電位(aV)と膜を挟まずに100mA/cm²の電流を流したときの電位(bV)を測定した。陽イオン交換膜の電気抵抗は次式により求めた。

【0041】

$$\text{電気抵抗} = 1000 \times (a - b) / 100 \quad [\Omega \text{cm}^2]$$

(3) 含水率

陽イオン交換膜を1mol/L-HClに4時間以上浸漬し、水素イオン型とし、イオン交換水で十分に水洗した後、膜を取り出しキムワイプ等で表面の水分を拭き取

り湿润時の重さ(Wg)を測定した。次に、膜を60°Cで5時間減圧乾燥させ乾燥時の重さ(Dg)を測定した。陽イオン交換膜の含水率は次式により求めた。

【0042】

$$\text{含水率} = 1000 \times (W - D) / D \quad [\%]$$

(4) ガス透過係数

ガス透過係数の測定方法として、U字管式水銀マノメーター(JIS Z 1707に準拠)によるガス透過試験機を用いた。測定に用いた陽イオン交換膜は50°Cにおいて含水状態でガス透過試験機に装着した。また、測定に用いたガスは、50°Cにおいて飽和温度に保った酸素または水素を用いた。ガス透過係数は次式により求めた。

【0043】

$$P = (p / t) \times (1 / A) \times \{1 / (P_a - P_b)\}$$

P : ガス透過係数 (cm³ (STP) · cm · cm⁻² · s⁻¹ · cmHg⁻¹)

p : ガス透過量 (cm³ (STP))

t : 測定時間 (s)

l : 陽イオン交換膜厚み (cm)

A : ガス透過面積 (cm²)

P_a : 高圧側ガス圧力 (cmHg)

P_b : 低圧側ガス圧力 (cmHg)

(5) 燃料電池出力電圧

ポリテトラフルオロエチレンで殺水化処理した空孔率80%のカーボンペーパー上に、白金30重量%の担持のカーボンブラックとパーカーフルオロカーボンスルホン酸のアルコールと水の5%溶液(デュポン社製、商品名ナフイオン)を混合したものを塗布し80°Cで4時間減圧乾燥しガス拡散電極とした。

【0044】次に、測定する陽イオン交換膜の両面に上記のガス拡散電極をセットし、150°C、圧力100kg/cm²の加圧下で100秒間熱プレスした後、室温で2分間放置した。これを図1に示す燃料電池セルに組み込み、圧力2気圧、燃料電池セル温度50°C、加湿温度50°Cの酸素と水素をそれぞれ200mL/min、400mL/minのときの出力電圧を測定した。

(6) 耐熱性(収縮率)

50°Cの乾燥機中で1時間予備乾燥させた測定用サンプル膜を160°Cの乾燥機中に30分放置した後、乾燥機から取り出して寸法を測定し、以下の式により収縮率を求めた。

$$S = 100 \times (L_a - L_b) / L_a$$

S : 収縮率 (%)

L_a : 50°Cの乾燥機中で乾燥させた膜の長さ (cm)

L_b : 160°Cの乾燥機中で30分放置した膜の長さ (cm)

実施例1～6

表1に示した組成表に従って、各種単量体等を混合して単量体組成物を得た。得られた単量体組成物400gを

500 mLのガラス容器に入れ、重量平均分子量35万のポリオレフィン系多孔質膜（A、B、C、各20 cm × 20 cm）を浸漬した。

【0046】次に、ガラス容器を真空ポンプで0.7 kPaの圧力まで10分間減圧にして減圧脱気した後、常圧に戻してポリオレフィン系多孔質膜の空孔に単量体組成物を充填した。続いて、ポリオレフィン系多孔質膜を単量体組成物中から取り出し、100 μmのポリエチルフィルムを剥離剤としてポリオレフィン系多孔質膜の両側を被覆した後、3 kg/cm²の窒素加圧下、80°C 5時間加熱重合した。

【0047】得られた膜状物を98%濃硫酸と純度90%以上のクロロスルホン酸の1:1混合物中に40°Cで45分間浸漬し、スルホン酸型陽イオン交換膜を得た。

【0048】これらのスルホン酸型陽イオン交換膜の膜厚、陽イオン交換容量、電気抵抗、ガス透過係数、燃料電池出力電圧、耐熱性を測定した。これらの結果を表2に示した。

【0049】比較例1

実施例1と同じ単量体組成物400 gを500 mLのガラス容器に入れ、分子量200万のポリオレフィン系多孔質膜（D）を大気圧下で10分間浸漬した以外は実施例1と同じ操作を行いスルホン酸型陽イオン交換膜を得た。

【0050】これらのスルホン酸型陽イオン交換膜の膜厚、陽イオン交換容量、電気抵抗、ガス透過係数、燃料電池出力電圧、耐熱性を測定した。これらの結果を表2に示した。

【0051】比較例2

ポリオレフィン系多孔質膜（A）を平均分子量20万のポリスチレンの10%ベンゼン溶液に5分間浸漬した。その後、液中からポリオレフィン系多孔質膜を取り出し、50°Cで乾燥した。この操作を5回繰返した後、10 0°Cで2時間減圧乾燥し膜状物を得た。

【0052】得られた膜状物を98%濃硫酸中に40°Cで60分間浸漬し、スルホン酸型陽イオン交換膜を得た。

【0053】これらのスルホン酸型陽イオン交換膜の膜厚、陽イオン交換容量、電気抵抗、ガス透過係数、燃料電池出力電圧、耐熱性を測定した。これらの結果を表2に示した。

【0054】比較例3

ペーフルオロカーボンスルホン酸膜（市販品）を用い、同様に膜厚、陽イオン交換容量、電気抵抗、ガス透過係数、燃料電池出力電圧、耐熱性を測定した。これらの結果を表2に示した。

【0055】

【表1】

実施例No.	多孔質膜 ¹⁾	組成			
		S t ²⁾	D V B ³⁾	A T B C ⁴⁾	P O ⁵⁾
1	A	60	40	15	5
2	B	60	40	15	5
3	C	60	40	15	5
4	A	80	20	10	5
5	B	80	20	10	5
6	C	80	20	10	5
比較例1	D	60	40	15	5

1) 多孔質膜

A ; ポリエチレン製、膜厚25 μm、空隙率45%、平均孔径0.5 μm

B ; ポリエチレン製、膜厚50 μm、空隙率60%、平均孔径0.5 μm

C ; ポリエチレン製、膜厚25 μm、空隙率80%、平均孔径0.5 μm

D ; ポリエチレン製、膜厚50 μm、空隙率60%、平均孔径0.5 μm

2) スチレン

3) ジビニルベンゼン

4) アセチルクエン酸トリブチル

5) t-ブチルバーオキシエチルヘキサノエート

【0056】

【表2】

実施例No.	膜厚	イオン交換容量	含水率	電気抵抗	水素ガス透過性×10 ⁸	酸素ガス透過性×10 ⁸	燃料電池電圧	耐熱性収縮率
1	30	1.1	48	0.05	2.5	1.5	0.62	10.3
2	64	1.5	52	0.07	2.2	1.3	0.60	11.5
3	90	2.3	62	0.10	1.9	0.9	0.55	12.8
4	28	1.5	55	0.04	2.8	1.9	0.56	11.4
5	60	2.3	70	0.05	2.4	1.4	0.56	13.4
6	82	2.9	83	0.09	2.1	1.1	0.66	13.6
比較例1	55	0.4	20	0.40	11.3	9.2	0.32	9.3
比較例2	30	0.4	15	0.30	20.2	15.2	0.28	10.4
比較例3	175	0.9	0.9	0.32	3.5	2.4	0.21	12.9

膜厚[μm]

イオン交換容量[mmol l/g-乾燥膜]

電気抵抗[Ω·cm²]

含水率[%]

水素ガス透過性[cm³ (STP) cm cm⁻² s⁻¹ cm H g⁻¹]酸素ガス透過性[cm³ (STP) cm cm⁻² s⁻¹ cm H g⁻¹]

燃料電池出力電圧[V]

収縮率[%]

【0057】

【図面の簡単な説明】

【図1】図1は、固体高分子電解質型燃料電池の基本構造を示す概念図である。

【符号の説明】

1 ; 電池隔壁

2 ; 燃料ガス流通孔

3 ; 酸化剤ガス流通孔

4 ; 燃料室側ガス拡散電極

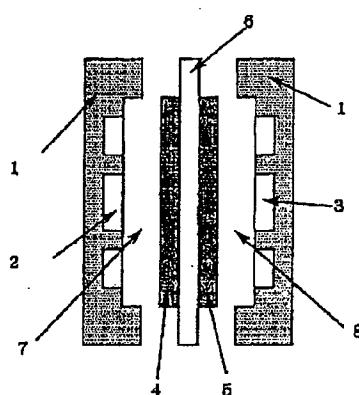
5 ; 酸化剤室側ガス拡散電極

6 ; 固体高分子電解質

7 ; 燃料室

20 8 ; 酸化剤室

【図1】



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